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(71) Applicant(s)  
**Cray Valley Limited**

**(Incorporated in the United Kingdom)**

**Waterloo Works, Machen, NEWPORT, Gwent,  
NP1 8YN, United Kingdom**

(72) Inventor(s)  
**Stephen Anthony Hall**

(74) Agent and/or Address for Service  
**Marks & Clerk  
57-60 Lincoln's Inn Fields, LONDON, WC2A 3LS,  
United Kingdom**

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US 4500696 A US 4093674 A**

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(54) **Powder coating compositions**

(57) A powder coating composition comprises a powdered solid ethylenically unsaturated material having a melting point from 60 to 120°C and obtainable by reacting an aliphatic or aromatic diisocyanate with an at least stoichiometric amount of an alcoholic component comprising a monohydric alcoholic component alone or in admixture with the dihydric alcoholic component, at least a part of the alcoholic component being ethlenically unsaturated, together with a curing system for the ethylenically unsaturated powdered solid material.

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POWDER COATING COMPOSITIONS

This invention is concerned with improvements in and relating to powder coating compositions and processes using such compositions.

Powder coating is a well-established process, basically comprising the application of a powdered fusible material to a substrate, heating of the powder in contact with the substrate to cause the the powder to melt and reflow, and cooling the resultant melt to form a solid coating on the substrate. The coating material may simply comprise a film-forming thermoplastic material or may comprise a reactive material, e.g. an epoxy resin together with a curing agent therefor, so that during the course of melting and reflowing reaction occurs to cure the material in situ on the substrate. In any event, powder coating materials are generally such that they have to be melted and reflowed at relatively high temperatures; e.g. 150°C or more. As a result, powder coating processes are generally not suitable for the coating of heat-sensitive materials such as wood or plastics material. In order to coat such materials, it would be necessary to have a product which had a relatively low melting temperature, e.g. below, say, 100°C, whilst at the same time being solid

at ambient temperature, which material could subsequently be cured in situ on the substrate during the melting/reflowing stage or, afterwards.

It has now been found, in accordance with the present invention, that useful solid ethylenically unsaturated materials, having relatively low melting point and suitable for use in powder coating compositions may be prepared by reacting a diisocyanate with one or more monohydric alcohols, optionally in combination with a dihydric alcohol.

According to one embodiment of the invention, therefore, there is provided a powder coating composition comprising a powdered solid material having a melting point of from 60 to 120°C and obtainable by reacting an aliphatic or aromatic diisocyanate with an at least stoichiometric amount of an alcoholic component comprising a monohydric alcoholic component alone or in admixture with a dihydric alcoholic component, at least a part of the alcoholic component, preferably the monohydric alcoholic component, being ethylenically unsaturated.

In accordance with a preferred embodiment of the invention the diisocyanate is reacted with an at least stoichiometric amount of:-

- (i) a monohydric alcohol component; or
  - (ii) a monohydric alcohol component followed by another different monohydric alcohol component; or
  - (iii) a monohydric alcohol component, followed by a dihydric alcohol component, followed by a monohydric alcohol component; or
  - (iv) a dihydric alcohol component, followed by a monohydric alcohol component alone or in admixture with a dihydric alcohol component;
- the monohydric alcohol component(s) comprising a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol, at least a part of the monohydric alcohol component being ethylenically unsaturated; and the dihydric alcohol component comprising a dihydric aliphatic alcohol or a dihydric polyalkylene glycol and being used in an amount not more than 50% of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups on the diisocyanate.

As noted above, it is a requirement of the present invention that the material obtained (hereinafter simply referred to as an "oligourethane", "urethane acrylate" or "oligomer") have a melting point of from 60 to 120°C (The term 'melting point' as used herein means the melting point as determined by the ball and ring method). It should be noted that not all materials obtainable in accordance with the process outlined above

may have melting points in the desired range. However, of course, to determine the melting point of any particular material is a matter for simple routine experiment and trial.

Suitable diisocyanates for use in the preparation of the oligourethanes include toluene diisocyanate, diphenylmethane-4,4'-diisocyanate (MDI), hexamethylene-1,6-diisocyanate, naphthylene-1,5-diisocyanate, 3,3'-dimethoxy-4,4'-biphenyldiisocyanate, 3,3'-dimethyl-4,4'-biphenyldiisocyanate, phenylene diisocyanate, 4,4'-biphenyldiisocyanate, isophorone diisocyanate (IPDI), trimethylhexamethylene diisocyanate, and tetramethylene xylene diisocyanate. Of these diisocyanates, the aromatic diisocyanates are generally preferred and, in particular, isophorone diisocyanate has been found to give particularly useful oligourethanes.

A wide variety of monohydric aliphatic alcohols may be used to produce the oligourethanes, e.g.  $C_1$  to  $C_{22}$  alcohols. Typical etherified dihydric alcoholic materials which may be used as monohydric alcoholic component include propylene glycol methyl ether (PGME), dipropylene glycol methyl ether (DPGME), ethylene glycol butyl ether (EGBE), diethylene glycol butyl ether (DPGBE), tripropylene glycol butyl ether (TPGBE) and propylene glycol phenyl ether (PPL). The most

convenient source of ethylenic unsaturation in the alcohol component is a mono-esterified dihydric alcohol in which the esterifying acid is an ethylenically unsaturated acid (such as acrylic acid or methacrylic acid).

Dihydric alcohols which may be used include, for example, alcohols, ethylene glycol, polyethylene glycol (PEG 1500), polypropylene glycol (PPG 750, 1000 and 1500), trimethylene glycol, dipropylene glycol, methylpropanediol and 1,6-hexanediol.

The reaction between diurethane and monohydric/dihydric alcohol component is suitably carried out in the presence of a catalyst such as cobalt benzoate, lithium acetate, stannous octoate, ethylamine and dibutyl tin dilaurate.

The molecular weight of the final oligourethane is suitably from 500 to 3000, preferably from 500-1500.

For some applications it is desirable that the oligourethanes be clear. It is not possible to predict whether any particular oligourethane produced in accordance with the invention will, or will not, have the desired optical properties in this respect. However, here again it is a matter of simple routine trial and experiment.

The ethylenically unsaturated solid material forming a part of the powder coating composition in accordance with the invention is in powdered form, e.g. has an average particle size of from 10 to 250, especially 10 to 90 microns. In addition to the particulate, ethylenically-unsaturated material, a powder coating composition in accordance with the invention comprises a curing system for the ethylenically unsaturated material.

In accordance with one embodiment of the invention, the curing system comprises a thermally initiated peroxide or like free radical-generating catalyst, optionally together with one or more promoters therefore. Suitable examples of such free radical-generating catalysts include 1,1-bis(t-butylperoxy)-3,5,5-trimethyl cyclohexane, 1,1-bis(t-butylperoxy)-cyclohexane, t-butylperoxy-isopropyl carbonate, t-butyl perisononanoate, t-butyl peracetate, t-butyl perbenzoate, dicumyl peroxide, di-t-butyl peroxide, t-butyl hydroperoxide, t-butyl perneodecanoate, diisooctanoyl peroxide, dibenzoyl peroxide, and azo bis(isobutyronitrile).

Preferably, the catalyst system is selected so that the powder can melt and reflow prior to curing. This makes it possible to obtain a level film, in contrast to

conventional epoxy/acid powders in which curing is effected during melting and reflowing, leading to an orange peel effect.

In accordance with another embodiment of the invention, the curing system comprises one or more photoinitiators, sensitive to ultraviolet light, optionally together with sensitizers therefore. By operating with such a system, the coating composition may be allowed to cool and solidify after melting/reflowing and then be subjected to appropriate irradiation to cure the coating. Examples of suitable photoinitiators/sensitizers include benzyldimethyl ketal, trimethylbenzophenone, isopropylthioxanthone, ethyl 4-dimethylamino benzoate, benzophenone, 2-chloro- and 2-ethyl-thioxanthone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-acetophenone, 2-hydroxy-2-methyl-1-phenyl-prepanone, 4-benzoyl-4'-methyl-diphenyl sulphide, 1-hydroxycyclohexyl-acetophenone, and 2-ethyl-hydroquinone.

Examples of suitable sensitizers include 4,4-dimethylamino-benzophenone, triethanolamine, N-methyl-diethanolamine, 2-(butoxy)ethyl 4-dimethylamino benzoate, and the products P104 (UCB), Photomer 4116 (Diamond Shamrock) and CN 381 (Santomer)



In accordance with a modification of the second embodiment of the invention, the curing system may be absent and curing of the solidified coating on the substrate may be effected by electron beam cure, which requires no initiator system.

In addition to the basic components noted above, coating compositions in accordance with the invention may, and often do, contain other ingredients particularly colorants such as pigments or dyestuffs. Other components which may be present include flow aids, anti-cissing agents, flexibilizers, degassing agents and inorganic fillers.

The invention also provides a powder coating process for coating a substrate which comprises applying a powder coating composition in accordance with the invention to the substrate, heating the composition to melt and reflow it on the substrate, and allowing the composition to cool on the substrate. In the case of the first embodiment of the invention discussed above, curing of the coating will preferably be effected by free radical polymerisation after the melting/reflowing step, whereas in the second embodiment of the invention an additional curing step is required, that is the substrate bearing the cured coating must be subjected to ultraviolet or electron beam radiation. Melting and/or

reflowing may be effected, for example, in an oven or by exposure to infra-red radiation.

In order that the invention may be well understood the following Examples are given by way of illustration only.

EXAMPLE 1

500g of isophorone diisocyanate and 0.2g of hydroquinone were charged to a 1 litre round bottomed flask which was fitted with a stirrer, thermometer, air sparge and an addition funnel. Heat was applied and the temperature was raised to 90°C with continued air sparging at a rate 1.51/hr. Upon reaching 90°C a mixture of 286g of hydroxyethyl methacrylate and 10.5g of hydroxyethyl acrylate was added to the contents over 1 hour. The temperature was then raised to 100°C and the isocyanate value was monitored until it falls below 165mgKOH/g which should usually take about 2 hours. Then 117.6g of neopentyl glycol was charged and the temperature was raised to 115 C, the temperature was maintained at 115°C with the air sparge at 1.51/hr until the isocyanate value fell below 30mgKOH/g and then 0.3g stannous octoate was added. The urethane will then exotherm to about 135°C and should be cooled back to 120°C at which temperature it is maintained until the NCO value falls to less than 30ppm. The urethane

acrylate was then discharged and allowed to cool. The material produced is a transparent, clear, tack free solid with a melting point of 77°C (B&R method) and a viscosity of 5.5 poise at 125°C (REL cone & plate viscometer). This material was called Resin A.

The following formulation was then mixed in a heated screw extruder using a screw speed of 250rpm to give a dwell time of the product in the extruder of 5 - 6 seconds. The product temperature was kept between 105 - 110°C with the wall temperature being maintained at 125 - 130°C.

Resin A	96.0
Flow Aid	3.8
(Monsanto Inc. Modaflow 2)	
2,2'-Azobisisobutyronitrile	0.2
(Wako Chemicals GmbH).	

This solid was then ground and classified to give a particle size of less than 90 microns and then sprayed onto a mild steel panel giving a film thickness of 15,µm. The panel was then placed in a fan assisted oven for 10 minutes at 100°C and then allowed to cool. Once cool the panel was seen to produce a perfectly levelled film with excellent adhesion, hardness and solvent resistance.

EXAMPLE 2

250g of diphenyl methane-4,4'-diisocyanate and 0.1g of dibutyl tin dilaurate was charged to a 1 litre round bottomed flask fitted with a thermometer, air. Sparge and an addition funnel. The contents were heated to 45°C and 37g of dipropylene glycol methylether were added and the temperature allowed to rise to 60°C. At 60°C, 67.5g of octadecanol was charged and the temperature raised to 110°C at which temperature 0.5g of hydroquinone was added. An air sparge was set at 1.51/hr and bubbled through the material while 116g of hydroxyethyl acrylate was added over 1hr while maintaining the batch temperature at 110°C until the isocyanate value falls below 30mgKOH/g. Then 33.5g of dipropylene glycol was charged and the batch temperature raised to 120°C and held until the NCO value is <30ppm. The urethane acrylate was then discharged and allowed to cool. It was found that the material produced was a very hard solid with a melting point of 101°C (B&R method) and had a extremely low viscosity of only 100 centipoise at 125°C (REL cone & plate). This material is called Resin B.

Resin B was extruded with 0.5% of a thermal initiator benzoyl peroxide and 2% of Modaflow, at a screw speed of 200rpm giving a residence time in the extruder of about 10 seconds. The temperature was

maintained between 110 - 115°C with the wall temperature between 120 - 125°C. The final product has a gel time of between 3 - 4 minutes at 110°C. The resultant material was then ground and classified to <90µm and electrostatically applied to a chromated aluminium test panel. The panel was then reflowed and cured in a fan assisted oven at 120°C for 10 minutes to yield a film with a Koenig hardness of 80% and a MEK swab resistance of >200 rubs.

### EXAMPLE 3

421.4g of isophorone diisocyanate and 0.15g of ethanox 703 (Ethyl S.A) was charged to a 1 litre round bottomed flask which was fitted with a stirrer, thermometer, nitrogen sparge and an addition funnel. The contents were then heated to 70°C, the nitrogen sparge set at a flow rate of 1.5l/hr and 148.1g of hydroxyethyl acrylate and 133.5g of neopentyl glycol added. The batch was then reheated to 70°C and allowed to exotherm to 125°C at which temperature it was maintained at. The isocyanate value was then monitored until it falls to less than 15mgKOH/g and 0.3g of stannous octoate added. The temperature was then raised to 130°C and held until the isocyanate value falls to <30ppm and then discharged and allowed to cool. A clear material was obtained that had a viscosity of 23.6p (Rel 150°C cone & plate) and a melting point of 103°C (B&R). This product was called Resin C.

Resin C was then extruded in the following formulation:

Resin C	91.0
Quantacure ITX (Ward Blenkinsop)	2.0
Irgacure 907 (Ciba Geigy)	3.0
P104 (UCB) 2.0	
Modaflow (Monsanto)	2.0

The screw speed of the extruder was set at 250rpm, batch temperature between 125-130°C and the wall temperature between 140-145°C, this gave a residence time in the extruder of about 7 seconds. The solid product produced was then kibbled and ground in a coffee grinder to give a fine powder. This was then sieved to a particle size of <90,µm. A 6" by 4" glass panel was then moistened with a water plus surfactant solution (washing up liquid) and the above powder applied to a film thickness of 40µm. This was then fully cured by exposure to UV light giving a film with a Koenig hardness 80% and a solvent resistance of >200 MEK rubs.

#### EXAMPLE 4

348g of toluene diisocyanate, 232g of hydroxyethyl acrylate, 122g 1,6-hexane diol and 0.2g ethanox 703 were charged to a round bottomed flask fitted with a stirrer, thermometer and a nitrogen sparge. The nitrogen sparge was set at 1.5l/hr and the temperature was allowed to rise from 20°C to 120°C without the application of heat. When the temperature reached 120°C heat was applied to

maintain the temperature and the isocyanate value was monitored until it fell to below 30ppm. The batch was then discharged and allowed to cool. A slightly coloured, clear product was obtained with a viscosity of 4.7 poise (Rel 125°C cone & plate) and a melting point of 64°C (B&R). This product was called Resin D.

500g of Resin D was reheated to 120°C and 15g benzophenone (BP ex Sartomer), 10g CN 381 (Acrylated amine synergist ex Sartomer) and 5g Modaflow (ex Monsanto). The material was then held at 120°C for 30 minutes and then discharged and allowed to cool. The product was Kibbled and ground up into a fine powder using a coffee grinder. It was then sieved and ground through a 90 m test sieve before being electrostatically sprayed onto a chromated aluminium test panel to a film thickness of 25µm. The test panel was then put in a fan assisted oven for 10 minutes at 95°C to reflow the powder, the panel was then removed from the oven giving a blemish free perfectly levelled film. The panel was then fully cured by exposure to UV light in a Spectral Minicure UV unit giving the following test results:

Koenig Hardness	75%
Adhesion (x-hatch)	100%
Reverse Impact	50"/lb Pass
	25"/lb Pass
Conical Bend	Pass
MEK resistance	>200rubs

EXAMPLE 5

392.3g of toluene diisocyanate, 178.4g of hydroxyethyl acrylate, 159.5g neopentyl glycol and 0.2g ethanox 703 were charged to a round bottomed flask fitted with a stirrer, thermometer and a nitrogen sparge. The nitrogen sparge was set at 1.5l/hr and the temperature was allowed to rise from 20°C to 135°C without the application of heat. When the temperature reaches 135°C heat was applied to maintain the temperature and the isocyanate value was monitored until it fell to below 30ppm. The batch was then discharged and allowed to cool. A slightly coloured, clear product was obtained with a viscosity of 8.4 poise (Rel 175°C cone & plate) and a melting point of 112°C (B&R). This product was called Resin E.

Resin E was then extruded in the following formulation:

Resin E	93.0	
Flow Aid	(Monsanto)	2.0
n-methyldiethanolamine	(BASF)	2.0
Lucirin TPO	(BASF)	3.0.

The screw speed of the extruder was set at 250rpm to give a residence time in the extruder of 8 9 seconds. The product temperature was kept between 130 - 135°C with the wall temperature maintained between 150 -



155°C. The solid product produced was then ground and classified to a particle size of <90 microns. The final powder had very good stability showing no cold flow at temperatures of upto 40 C.

A sapele veneered medium density fibre - board 19cm x 29cm x 0.5cm was lightly damped with water and sprayed with the above formulation to a film thickness of 30µm. The substrate was then placed in a oven for 10 minutes at 125°C to yield a completely levelled tack free film. The substrate was then twice passed through a Spectral Minicure UV unit with a belt speed of 5 metres per minute to raise the MEK resistance from 3 rubs to >200 rubs. The final film produced was then evaluated as follows:

Impact Test	BS3962 Part 6		4
Cross Hatch	Test BS3962 Part 6		4
Wet Heat	BS3962 Part 2	55°C	5
		70°C	5
		85°C	5
Dry Heat	BS3962 Part 3	85°C	5
		100°C	5
		120°C	5
		140°C	5
		160°C	5
Marking by Liquids	BS3962 Part 4	Acetone	5
		Butyl Acetate	5
		Toilet Spirits	5
		Potable Spirits	5
		Tea	5
		Coffee	5
Koenig Hardness			80%
MEK swabs			>200
Xylene swabs			>200
60% Gloss	Along Grain		95%
	Against Grain		95%
Scrape Test	BS3962 Part 6		4

Note: Composition of test liquids  
1. Toilet Spirits 8:1 (IMS:Water)  
2. Potable Spirits 1:1 (IMS:Water)

The system passes BS6250 general and severe ratings exhibiting extremely good hardness and resistance properties. The heat resistance is also extremely good. It also passes DIN 68861 group A (chemical resistance and stain tests).

## CLAIMS:

1. A powder coating composition comprising a powdered solid ethylenically unsaturated material having a melting point from 60 to 120°C and obtainable by reacting an aliphatic or aromatic diisocyanate with an at least stoichiometric amount of an alcoholic component comprising a monohydric alcoholic component alone or in admixture with the dihydric alcoholic component, at least a part of the alcoholic component being ethylenically unsaturated, together with a curing system for the ethylenically unsaturated powdered solid material.

2. A powder coating composition as claimed in claim 1 in which the powdered solid ethylenically unsaturated material is one obtained by reaction of an aliphatic or aromatic diisocyanate with an least stoichiometric amount of:

- (i) a monohydric alcohol component; or
- (ii) a monohydric alcohol component followed by another different monohydric alcohol component;
- (iii) a monohydric alcohol component, followed by a dihydric alcohol component, followed by a monohydric alcohol component; or
- (iv) a dihydric alcohol component, followed by a monohydric alcohol component alone or in admixture with a dihydric alcohol component.

the monohydric alcohol component(s) comprising a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol, at least a part of the monohydric alcohol component being ethylenically unsaturated; and the dihydric alcohol component comprising a dihydric aliphatic alcohol or a dihydric polyalkylene glycol and being used in an amount not more than 50% of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups on the diisocyanate.

3. A powder coating composition as claimed in claim 1 or claim 2 in which the curing system comprises a thermally initiated free radical-generating catalyst.

4. A powder coating composition as claimed in claim 1 or claim 2 in which the curing system comprises a photoinitiator sensitive to ultraviolet light.

5. A powder coating composition as claimed in claim 1 substantially as hereinbefore described.

6. A method of coating a substrate which comprises applying a coating composition as claimed in claim 3 to the substrate, heating the composition to melt and reflow it on the substrate, and allowing the composition to cool on the substrate.

7. A powder coating process for coating a substrate which comprises applying a powder coating composition as claimed in claim 4 to the substrate, heating the composition to melt and reflow it on the substrate, and allowing the composition to cool on the substrate, and subsequently curing the cooled coating by exposure to ultraviolet light.

8. A modification of the method claimed in claim 6 in which the coating composition contains no curing system and the cooled coating on the substrate is cured by exposure to an electron beam.

9. A method as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

**Patents Act 1977**  
**Examiner's report to the Comptroller under Section 17**  
**(The Search report)**

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**Relevant Technical Fields**

- (i) UK Cl (Ed.M) C3P - PDIE C3V - VCA  
 (ii) Int Cl (Ed.5) C09D

Search Examiner  
 MR M J PRICE

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 8 SEPTEMBER 1994

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-  
 1-9

(ii) ONLINE DATABASES: WPI

**Categories of documents**

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| <b>X:</b> Document indicating lack of novelty or of inventive step.   | <b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.        |
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| <b>A:</b> Document indicating technological background and/or state of the art.   | <b>&amp;:</b> Member of the same patent family; corresponding document.   |

Category	Identity of document and relevant passages		Relevant to claim(s)
X,Y	GB 1590413	(LORD) See the Claims and Examples	1 at least
X,Y	WO 93/19132	(DSM) See eg page 12 lines 20-28	1 at least
X,Y	US 5089586	(WOLFF) See the Claims and Examples	1 at least
X,Y	US 4500696	(HULS) See the Claims and Examples	1 at least
X,Y	US 4093674	(NIPPON) See the Claims and Examples	1 at least

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